Intermediate range order dynamics near the glass transition

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Abstract.   Correlations in the atomic structure and dynamics extend in glasses and (supercooled) liquids to an intermediate range, which is a few times longer than the interatomic spacing. Motion on this length scale can be expected to be particularly revealing of collective phenomena. However, due to neutron scattering experimental difficulties, namely to all-pervasive spurious multiple scattering effects and to the weakness of the signal at wave numbers corresponding to this length scale, very little is experimentally known so far about the dynamics in this range. We have developed a new experimental strategy to overcome these difficulties, and applied this novel approach to the study of the archetypal fragile glass former CKN. Our results provide the first direct experimental evidence for the existence of a first, fast structural relaxation step in the supercooled liquid phase, which does not scale with the viscosity and which cannot be attributed to extra vibrational modes, either propagating or local. The enhanced slowing down with decreasing temperature of the slow (α) relaxation process in the wave number domain of the intermediate range order also allowed us to investigate the temperature dependence of the amplitude of this relaxation step in a model independent manner. In contrast to some previous findings, our direct results show no sign of any critical singularity above the glass transition temperature.

1. Introduction

In the past decade inelastic neutron scattering played an important role in peeking into the secrets of the formation of glasses. This technique has the unique feature of allowing us to explore microscopic dynamics in condensed matter directly in space and time—at least in principle. In practice both ambiguities of interpretation and inescapable experimental difficulties present substantial limitations, particularly in studying matter without the very helpful crystalline symmetry. The present work was aimed at gaining ground against some of these limitations.

Under usual experimental conditions the particularly weak inelastic scattering signal at small wave numbers q is inextricably masked by spurious multiple scattering. By establishing a new technique to reliably overcome this difficulty, we were able to considerably extend the q range accessible for inelastic scattering work in glasses and liquids, typically to a dynamic domain of 1:15 (0.2 to 3 Å^{-1}), to be compared with the previous practical restriction $q > 0.8$–1.2 Å^{-1}, depending on the sample. This extension of the q range toward smaller values opens up a field of new opportunities in several respects. Interpreting the data inevitably involves comparison with a combination of different model contributions, and this can be done the more meaningfully the broader the domain of comparison is. In addition, models to be considered are often better approximations for small q values, i.e. on length scales larger than interatomic spacing, where details about individual atoms play a lesser role. For the same

reason, the decisive collective aspects, which ultimately must determine the global behaviour, are undoubtedly related to correlations on length scales beyond atomic spacing, even if there is no long-range order in glasses. It is quite likely that the key to understanding of phenomena in glasses is the understanding of the range, nature and evolution of the correlations on an intermediate length scale of several times nearest neighbour distances.

There is ample evidence for structural correlation on this length scale in a large variety of glasses, a subject that has been explored in great depth and referred to under various names by a large number of groups. As one example, figure 1 shows the elastic structure factor at various temperatures of the archetypal fragile glass former $Ca_{0.6}K_{0.4}(NO_3)_{1.4}$ (CKN) we have been investigating in this study. The maximum at $q \approx 0.8$ Å^{-1} is a clear signature of correlations beyond that between nearest neighbours (which latter is reflected by the main peak at $q \approx 1.8$ Å^{-1}) and following the literature it can either be called a 'pre-peak' or 'intermediate range order' or 'first diffraction peak'. It is worth keeping in mind that the first Bragg peak in the various crystalline forms of CKN appears around this q value of 0.8 Å^{-1}.
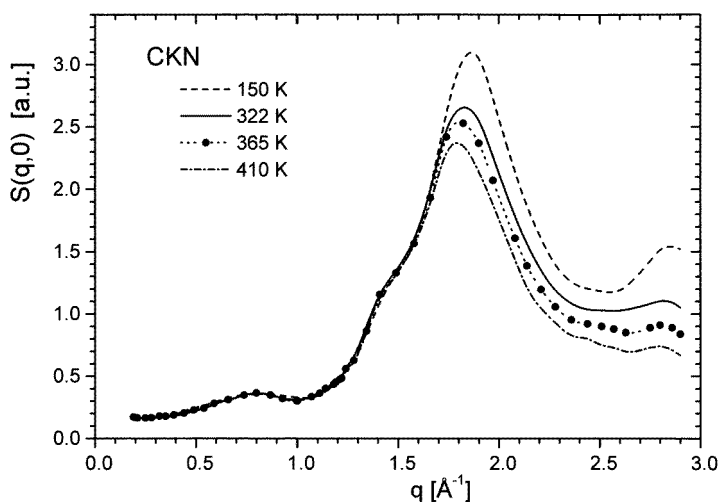

Figure 1. The elastic structure factor of CKN at various temperatures below and above the glass transition temperature $T_g \cong 333$ K. For clarity, the actual data points are only shown for one temperature. The 'elastic' intensity has been defined by ± 0.1 meV energy window around $\omega = 0$.

Our results show, indeed, that exploring the intermediate range order dynamics can offer new insight into what happens in glasses and liquids near the glass transition. In the extended q range one can more meaningfully probe the nature of the observed dynamic processes in space and time, notably to distinguish between vibrational features and structural relaxation. This allowed us to provide, for the first time, direct experimental evidence for the existence of a first, fast structural relaxation step above T_g, which cannot be explained by local or long wavelength vibrations. An indication of stronger collective effects on the intermediate range length scale is that the main structural relaxation process (α relaxation) is by close to an order of magnitude slower on this scale than on the nearest neighbour atomic scale. This allowed us to explore the amplitude of this process in a direct, model independent fashion and we have found no sign of any singularity indicative of the existence of a critical temperature above T_g. Both of our main findings concern long-standing controversies.

2. Fundamentals

In general terms, one difficulty of interpreting scattering results in disordered materials is that the measured dynamic structure is a vast average over several atomic species and an infinite number of local configurations. In a more distant future one can think that by combining molecular dynamics calculations with improved neutron scattering results, we will be able to obtain a full picture of atomic dynamics atom by atom. We are very far today from this level of understanding, and instead a few general rules of limited validity can be and are being used in order to extract information on the spatial characteristics of dynamical processes [1, 2]:

(a) For propagating vibrations of long enough wavelength, $\lambda \gg 2\pi/q$, the dynamic structure factor will behave for constant frequency (energy transfer) ω as $S(q, \omega = \text{const}) \propto q^2 S(q)$ (with $S(q) = \int S(q, \omega)\,d\omega$ being the static structure factor).
(b) For local vibrations one expects $S(q, \omega = \text{const}) \propto q^2$ in the low q limit, i.e. $q \ll 1/R$, where R is the spatial extent of the vibrating object.

It has to be noted that the derivation of rule (a) by Carpenter and Pelizzari [1] assumes that the Debye–Waller factor $e^{-2W} \cong 1 - CTq^2$ can be taken as equal to 1, i.e. that the temperature T is very low (C is a constant). This is not a good approximation for a supercooled liquid. Taking into account that $S(q)$ depends very little on temperature [3] and thus the integral of the inelastic processes has to scale as $1 - e^{-2W} \propto q^2$, one can expect that the form given in (a) remains valid even if e^{-2W} is substantially different from one. This implies that both single and multiple phonon processes are being considered (as they should), with the single phonon contribution expected to be proportional to the elastic structure factor as $q^2 S(q, 0)$. In what follows we take the lowest temperature curve in figure 1 as the experimental static structure factor $S(q)$, once corrected for thermal expansion.

The limited applicability of rules (a) and (b) is illustrated in figure 2, in which $S(q, \omega)$ is compared for polycrystalline and glassy CKN at 250 K. The little difference observed between the two phases shows that at energies comparable to 10 meV the q dependence of $S(q, \omega)$
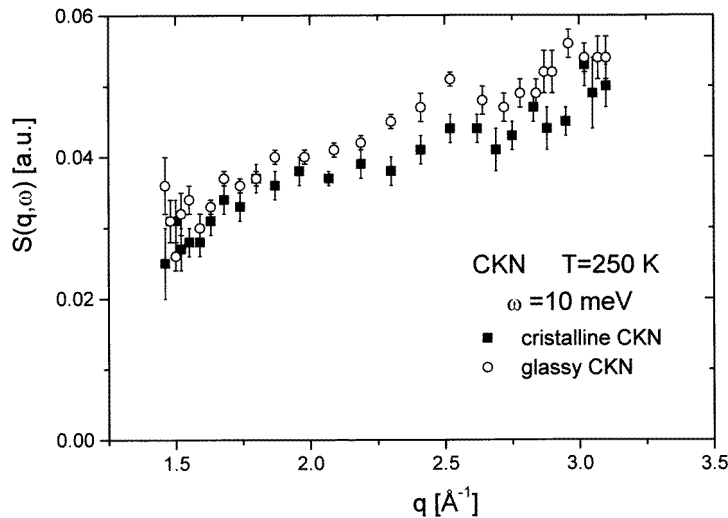

Figure 2. Comparison of the observed wavenumber dependence of the dynamic structure factor at constant energy $\omega = 10$ meV between crystalline and glass phases of CKN.

is hardly sensitive to the propagating (in the crystal) or non-propagating character (by all expectation in the glass at this energy) of the excitation. It is also obvious that this excitation energy is by far too high for the $q^2S(q)$ rule to be valid. Note that the powder pattern of the crystalline material 'smoothed' over nearby Bragg peaks closely reproduces $S(q,0)$ of the glass. The breakdown of rules (a) and (b) is to be expected since the approximate assumptions behind them include two conditions obviously not fulfilled for energies not negligible compared to the Debye temperature. Namely, the variations of $S(q)$ cannot be neglected over the range $q \pm 2\pi/\lambda$, where λ is the wavelength of the excitations and it can be estimated based on the sound velocities to be about 0.4 and 0.8 Å^{-1} for longitudinal and transverse modes, respectively. Furthermore, the polarization vector of the vibrations will not be the same for all atoms of different species and with different neighbours. In view of figure 2 and these considerations one has to question the validity of a series of recent studies aimed at determining the density of states of localized and propagating vibrational modes on the basis of these rules (a) and (b) at energies comparable to 10 meV. Molecular dynamics calculations have also shown [4] that all vibrational modes in a glass in reality reveal both kinds of feature simultaneously and cannot be divided into the categories of propagating (or in-phase) and localized (or random phase) excitations.

On the other hand, at smaller wave numbers and energies one can expect rule (a) to well describe the behaviour of sound waves in the glass phase. The difficulty of experimentally observing this is the overwhelming multiple scattering contribution in the neutron scattering spectra taken under customary conditions at small q values. The results in figure 3 show $S(q, \omega)$ in CKN in the constant energy window 0.45 ± 0.1 meV at a temperature below the glass transition point. Three different neutron wavelengths have been used in order to cover a wide q range and, as will be discussed in the next chapter, to allow us to perform a precise correction of the raw spectra for the combination of multiple scattering, absorption and scattering self-screening, by using the new technique we have just developed. The data were collected at the time-of-flight (TOF) spectrometer NEAT at BENSC, HMI, Berlin and detailed account of the experiment will be published elsewhere [5]. The results in figure 3 illustrate that indeed, in contrast to figure 2, at small excitation energies the $q^2S(q)$ rule well describes
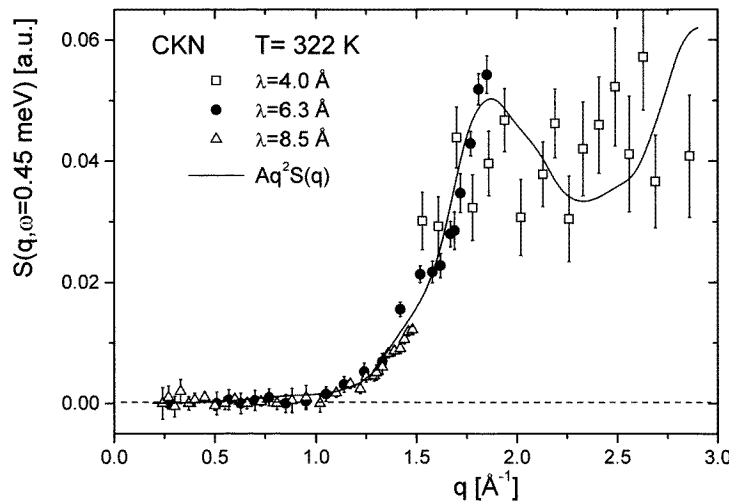

Figure 3. Wavenumber dependence of the dynamic structure factor integrated over the energy window 0.35–0.55 meV in the glass phase. The line represents a fit by the model function $Aq^2S(q)$, where the coefficient A was the only adjustable parameter.

inelastic scattering spectra in CKN in the glass phase, which is consistent with the assumption that sound waves play a dominant role here. (The high energy resolution needed in this work at each wavelength was, of course, the hardest to achieve at the shortest wavelength, which explains the lower statistical accuracy of the 4 Å data.)

3. The key to exploring small q values: correction for multiple scattering

Multiple scattering (MS) can be in principle made negligible by using very thin samples. Another common technique for its reduction is to introduce Cd plates into the sample parallel to the scattering plane in order to intercept scattered neutrons propagating at a high angle to this plane. Both methods reduce the scattered beam intensity and fail by far to sufficiently eliminate MS before the intensity reduction becomes prohibitive. We are left with the only choice of living with a non-negligible amount of MS and learning to determine it with an accuracy that does not compromise the precision of the determination of even very weak single scattering signals. We have achieved this by developing an experimental strategy combining two procedures: (a) taking scattering data at various wavelengths, i.e. with various amounts of MS, and (b) numerically simulating the MS contributions to a high degree of precision.

Indeed, in view of the shape of both the elastic (figure 1) and inelastic (figure 3) structure factors, it is obvious that in amorphous matter the amount of MS strongly depends on the incoming neutron wavelength, an effect similar to the Bragg cut-off in polycrystalline materials. The three as-measured spectra $S_m(q, \omega)$ shown in figure 4 (already corrected for background, detector efficiency and normalized to vanadium standard scatterer) strikingly illustrate this phenomenon in the form of mutual inconsistency at $q < 1.2$ Å^{-1}. In actual fact, multiple scattering is the weakest at 8.5 Å incoming wavelength, since in this case few of the high intensity parts of the spectrum are accessible in a scattering process: the largest possible momentum transfer at 0.45 meV energy gain is 1.61 Å^{-1}, achieved in exact backward scattering. The leading contributions to MS are combinations of one elastic and one inelastic

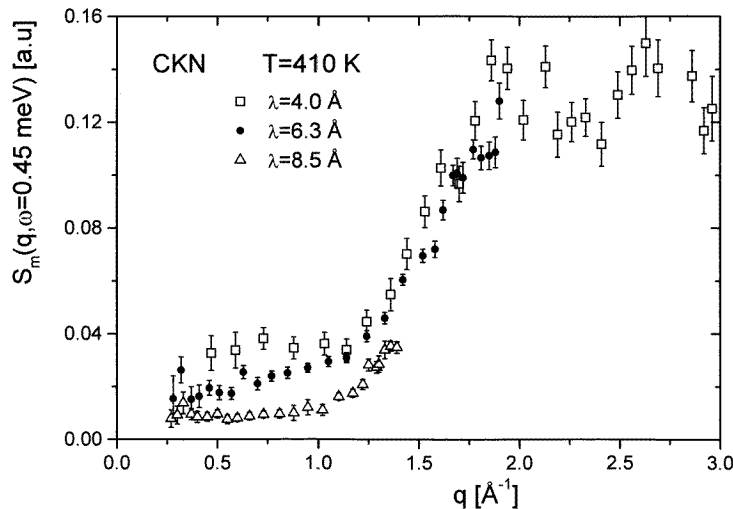

Figure 4. Measured apparent dynamic structure factor using different incoming neutron wavelengths. The large differences at low q are due to different amounts of multiple scattering contamination at each wavelength.

event, both corresponding to scattering at high angles. The very high multiple scattering contribution at 4 Å wavelength is due to additional double scattering processes involving neutrons scattered once inelastically on the sample and once elastically on the lowest order Bragg peak of Al ($q = 2.69$ Å^{-1}), which is the material of the sample holder and of various parts of the cryofurnace surrounding the sample.

The simplest tentative correction for multiple scattering is to assume that all scattering at small q has its origin in multiple scattering and to subtract a corresponding, q independent constant from the spectra. (It can indeed be shown by numerical model calculations that the multiple scattering contributions tend to be constant in the lower third of the q range accessible at a given incoming wavelength, and they usually smoothly decrease towards higher q). This approach is the one most commonly used and, of course, by being based on the assumption that what is observed at small q is the multiple scattering contribution, it denies by itself all possibility to collect any useful information in the q range typically below 1 Å^{-1}.

Our technique of correcting for MS follows the following fundamental idea. We explore the lowest q range primarily by using long neutron wavelengths, in order to make the MS effects small. Additional shorter wavelength measurements allow us to explore the higher q range, which information is also needed as input for the numerical simulation for correcting the long wavelength spectra, where the corrections are relatively modest. Using the same calculation for correcting spectra taken at shorter wavelength also serves as a consistency check of the procedure, which should make all data coincide over the range of their meaningful overlap. The need for this novel multi-wavelength approach is well illustrated by the data in figure 4. The single scattering contribution at 8.5 Å wavelength proved to be about 70% of the observed signal at $q < 1$ Å^{-1}; it only amounts to about 20% at 6.3 Å. While it is possible to use an exact algorithm (as we do) for simulating neutron trajectories, absorption and subsequent scattering events in a sample of precisely known geometrical shape, some uncertainty will always remain concerning the model sample scattering function used in the calculation, even after any number of steps of self-consistent refinement. This uncertainty will always be much too high for credibly extracting a 20% signal masked by 80% MS noise. Note that correction for sample absorption and scattering self-screening cannot be correctly performed independently of multiple scattering effects, so all these three distortions must be taken care of by the simulation calculation simultaneously.

For the numerical simulation we need to establish a model for $S(q, \omega)$, including in particular the largest contribution from elastic scattering, $S(q, 0)$, Here $\omega = 0$ means 'within the energy resolution of the instrument'. At all temperatures studied in this work the real line width of what appeared to be 'elastic' in the TOF experiment remained less than 0.3 μeV (as determined by high resolution neutron spin echo (NSE) spectroscopy), i.e. less than 0.6% of the TOF resolution. In the first iteration $S(q, \omega)$ was taken as the as measured apparent $S_m(q, \omega)$ obtained at each q value by using the longest incoming wavelength (i.e. the one least affected by MS) which still made this q accessible in view of the limited useful range of scattering angles <120°. For example in the case shown in figure 3 this meant to take the 8.5 Å data up to $q = 1.35$ Å^{-1}, the 6.3 Å data up to $q = 1.8$ Å^{-1} and the 4 Å data above. Since we found no way to gather enough information for modelling multiple scattering effects involving Bragg scattering on Al cryostat (and spectrometer) parts, the 4 Å data were corrected by the conventional 'subtraction of a constant' method. In a sequence of iteration steps the model was refined on the basis of comparing the numerically simulated scattering spectra with the measured ones (for the two longer wavelengths), and convergence (within error full reproduction of the measured data) was achieved in not more than three iteration steps. The final corrected data were then determined by computing the difference between the measured and ideal single scattering spectra using the model function obtained as the result of

the iteration. Note that, as mentioned above, the exact correction for sample absorption can only be performed as part of this procedure, i.e. by simultaneous numerical modelling of both multiple scattering and absorption.

This procedure requires the exact knowledge of the absolute probability of scattering and absorption in the sample. We have achieved this by experimentally determining the transmission coefficient of the sample in a broad wavelength range, which is at some wavelengths dominated by scattering effects as opposed to absorption. The absorption cross section could be calculated with sufficient precision from tabulated values. For samples with higher absorption (in CKN the neutron absorption range is several cm) the absolute scattering probabilities are best determined by comparison to a V standard, after careful multiple scattering and absorption correction of both the V and sample spectra. Our approach is generally applicable for all amorphous samples, and it opens up a whole field of new opportunities in the study of glasses and liquids by making a potentially very important wavenumber range for the first time accessible to inelastic neutron scattering work.

As an example, the final, absorption, self-screening and multiple scattering corrected results for the measured spectra shown in figure 4 are given in figure 5. It is evident, on the one hand, that data taken at 8.5 and 6.3 Å wavelengths now coincide within error, which is a crucial consistency criterion. (As mentioned above, the 4 Å data could not be corrected exactly; insuring coincidence at small q by subtracting a constant was in this case the correction itself.) It is also apparent that, at this temperature, well above T_g, $S(q, \omega)$ drastically deviates from the $q^2 S(q)$ rule.
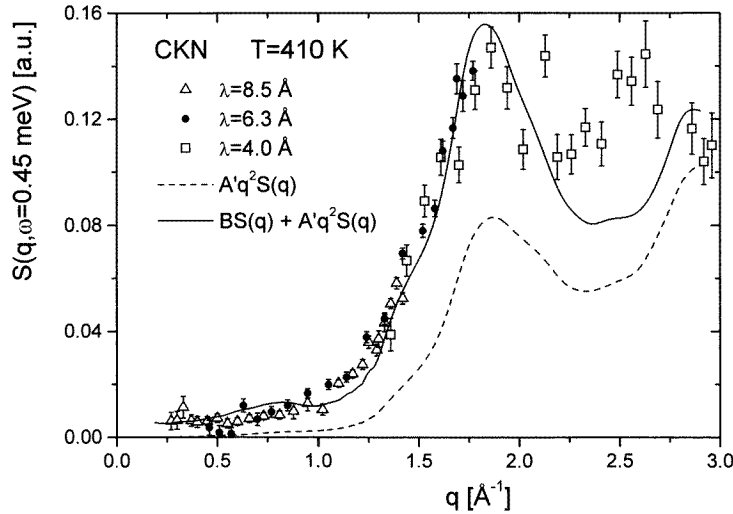

Figure 5. Data shown in figure 4 after correction for multiple scattering, absorption and scattering self-screening show the unambiguous signature of structural relaxation (see text). The dashed line corresponds to the line in figure 3 scaled to 410 K by a coefficient $A' = 1.3 A n_B (410 \, \text{K})/n_B (310 \, \text{K})$, where the factor 1.3 takes into account the anharmonicity (see text) and n_B is the Bose factor. The coefficient B was the only adjustable parameter in obtaining the solid line.

4. Direct evidence for a fast component in the structural relaxation

The evolution of the dynamic structure factor with temperature is illustrated in figure 6. The $q = 1.45 \, \text{Å}^{-1}$ spectra shown here are representative of all q values observed, with variations
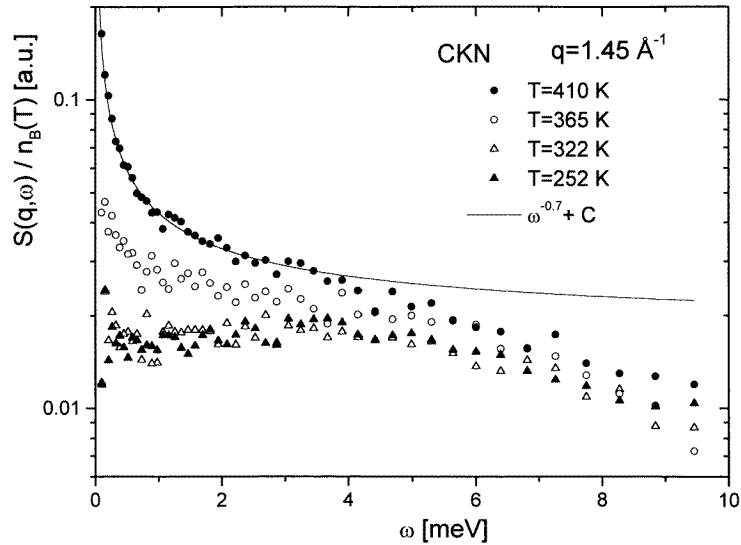
Figure 6. Bose factor normalized spectra at a representative q value below and above $T_g \approx 333$ K. The line illustrates that the quasielastic contribution emerging above T_g can be represented by a self-similar power law for $\omega < 3$ meV. The constant C was fixed as $C = 0.017$, in order to represent the low temperature spectra. Equally good fits can be obtained, for example, at $C = 0$ with an exponent of -0.55, or at $C = 0.022$ with an exponent of -0.85.

of proportions which will come to light in what follows. The spectra are normalized to the Bose temperature factor. Below $T_g \cong 333$ K we observe a nearly Debye type behaviour ($S(q = \text{const}, \omega) = \text{const}$) up to about 6 meV with a boson peak maximum at about 3.5 meV. The temperature dependence is in a good approximation harmonic, with a sign of a slight anharmonicity (not exceeding the error) below 2 meV. This latter trend became actually only apparent by inspecting the totality of the spectra taken at different q. Both the observations of the boson peak and of this slight anharmonicity are new in neutron scattering on CKN. They actually are in agreement with light scattering results [6], in which case, due to the different coupling, these features are more salient. In view of its quasi-perfect harmonicity, the spectra below 333 K can be attributed to vibrations, which is in agreement with our finding on the q dependence, as discussed above in connection with figure 3.

Above T_g the evolution of the spectra becomes anharmonic, namely in a dramatic fashion below 3 meV, as it already has been found before in every more or less fragile glass, including CKN. In this energy range the data can be represented by a constant corresponding to the harmonic spectra below T_g and an extra contribution of the shape of a power law, as indicated in the figure. This particular, self-similar shape means that this contribution, which we will refer to as the 'β process', cannot be characterized by an energy width, although there must clearly be a cut-off energy on the high energy side, in order to avoid divergence of the integrated intensity. This cut-off energy actually appears to be around 3 meV, where the power law stops being applicable and the intensity gradually drops to zero. This β process is the dominant feature of $S(q, \omega)$ in the energy window shown in the figure. At these temperatures the well known α structural relaxation process, whose characteristic rate scales with the viscosity, appears on an energy scale at least two orders of magnitude smaller. The situation is illustrated in figure 7, where the temporal decay of the instantaneous correlations is represented by the intermediate scattering function as measured directly by neutron spin echo (NSE) in the time

window 20–1000 ps, and computed as $I(q, t) = \int S(q, \omega) \cos(\omega t) \, d\omega$ in the time window 0.05–6 ps, which corresponds to the energy range shown in figure 6. (Note that due to detailed balance at these temperatures $I(q, t)$ can be taken as a real function.) The data from the two different kinds of measurement have been somewhat arbitrarily joined together in a smooth fashion, as illustrated by the dashed portion of the line. We had no other option, since on the NSE spectrometer one cannot obtain an accurate integral over the high energy part of the spectra (below about 0.3 ps in time, i.e. above 2.2 meV in energy). Nevertheless, we expect the curves in figure 7 to be exact within 1–2%. The NSE results could be well represented by a Kohlrausch function with exponent 0.6. We will come back to various features shown in this figure later in the discussion; at this point we just want to observe that the α and β processes are pretty well separated at the temperatures we are concerned with here.
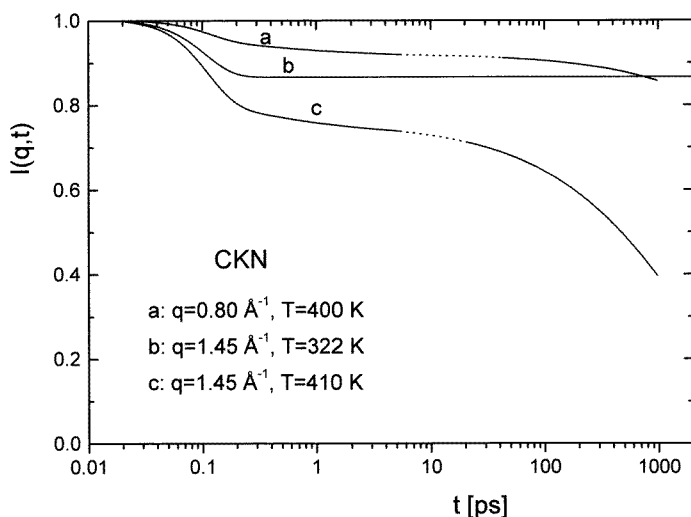

Figure 7. Sample intermediate scattering functions (relaxation functions) obtained by Fourier transformation of the TOF data (covering the time domain 0.01–6 ps) joined by extrapolation (dashed lines) to smoothed curves proportional to the directly measured NSE data at $t > 20$ ps (see text). In the glass phase (b) the curve is known to be flat for $t > 1$ ps, i.e. beyond the range of vibrational contributions.

One of our main goals in this work was to study the nature of the β process by exploiting its q dependence in an up to now inaccessibly broad q range, i.e. including that of the intermediate range order. The behaviour of $S(q, \omega = \text{const})$ above the glass temperature $T_g \cong 333$ K, as shown in figure 5 at 410 K (and representative of all four energy groups below 1 meV we have evaluated) is drastically different at low q from the one in figure 3. Namely, the spectra cannot be described for $q < 1.2$ Å^{-1} by either a $q^2 S(q)$ or a q^2 law, or a combination of these rules, although these rules are precisely expected to best hold for vibrational contributions at the small energy and low q values we are concerned with. If we tried to assume that we are concerned with localized vibrations for which the q^2 rule is no longer valid for $q > 0.3$–0.4 Å^{-1}, we would effectively assume that the size of the rigidly and 'locally' vibrating object is larger than some 10–20 Å. On this kind of length scale the atomic motion can be correctly represented by continuum hydrodynamics. Collective motion of chunks of material of this size corresponds to nothing that can be regarded as local atomic vibration, but rather to random flow, or, in other words, structural relaxation, i.e. the loss with time of memory of *all* atomic positions within

the range of correlations related to the instantaneous order, as reflected by the structure factor $S(q)$. In a first approximation $S(q, \omega = \text{const})$ is found to be proportional to $S(q)$ in the q range below 1.2 Å^{-1} (cf figure 5), which is an approximate, qualitative feature of structural relaxation [2].

This finding is the first direct experimental evidence that in supercooled liquids the structural relaxation consists of two, at low enough temperatures in the time domain well-separated, steps. The existence of two structural relaxation stages has been theoretically predicted [7, 8]. It is a most fundamental feature of mode coupling theories (MCT) [7], and the present results thus lend a strong experimental support to this theoretical approach. The two step structural relaxation is a direct consequence of the non-linear feedback introduced in MCT by allowing the viscosity to depend on the density–density correlations. Our conclusion is at variance with the point of view expressed in previous experimental studies of other fragile glasses, e.g. [9], namely that the β process is vibrational in character and probably corresponds to long wavelength excitations. Those studies explored a much more limited q range around the main peak of the structure factor only. In view of the marked similarity observed by now in all experimental studies of fragile glasses of very different types of material, we conjecture that the predominantly structural relaxational character of the β process is a general feature of supercooled liquids near the glass transition.

While the data in figure 5 unambiguously show that structural relaxation is the dominant contribution at small q in the range of the intermediate scale order, it is much harder to infer the role of this process at q around the main peak of the structure factor. (This is just another aspect of the notorious difficulty of interpreting spectra restricted to this higher q range.) The dashed line in figure 5 represents a tentative extrapolation of the contributions from long wavelength vibrational modes based on the data in figures 3 and 6. In the latter figure one can observe that the spectra at $\omega > 5$ meV, i.e. above the energy domain of the β process, show some deviation from harmonic temperature dependence, which amounts to about 30% excess intensity at 410 K compared to Bose scaling. This degree of anharmonicity in going over into the liquid phase is not unexpected; actually a softening of the sound waves also takes place. The difference in figure 5 between the measured spectrum and the vibrational contribution so estimated (dashed line) is found to roughly follow the elastic structure with some oscillations around it (cf continuous line in the figure). These oscillations clearly correlate with the previously observed pronounced de Gennes type narrowing in the q dependence of the characteristic time of the slow stage of structural relaxation (α process) [10]. This similarity appears to be quite plausible: the slowing down of the structural relaxation at q corresponding to the strongest atomic correlations (diffraction peaks) is indicative of the enhanced stability of these correlations. This stability can offer the reasonable explanation for the minima in the strength of the fast (β) step in structural relaxation, the strongest one appearing at the first diffraction peak (intermediate range order), surrounded by a maximum on each side. A very similar oscillatory behaviour of the amplitude of the β relaxation process normalized to $S(q)$ has also been theoretically predicted by MCT [7].

To summarize, the main conclusions in this chapter are that our experimental results show for the first time that the characteristic quasielastic scattering contribution emerging above T_g in all more or less fragile glasses in the energy domain around 1 meV is (a) overwhelmingly due to a first, fast step in the structural relaxation (as opposed to vibrational modes) at wave numbers around the region of the intermediate range order in CKN, and (b) this process might fully account for the quasielastic contribution in question over the entire q range of interest, including the region of the main peak in the structure factor. These properties exactly correspond to those of the β process of MCT, and exclude all interpretations by models based on propagating or local vibrational modes. It is our conjecture, in view of the impressive

similarity of the dynamics in many fragile glasses, that these conclusions most likely hold not only for CKN but for most or all more or less fragile glass formers.

5. Absence of model independent signature of a critical temperature $T_c > T_g$

Previously reported experimental evidence for a critical temperature predicted by MCT was obtained by extracting a set of parameters in a process of fitting the observed spectra by predicted line shapes and scaling properties. Unfortunately, the number of adjustable parameters is substantial, and while this kind of approach has successfully confirmed the *compatibility* of MCT predictions and experiment, it cannot deliver an *unambiguous* proof of the correctness of these predictions. The exploration of the intermediate range order dynamics can also be expected to provide additional new insight into this question. On the one hand side, on this length scale, as pointed out above, the relative role of the collective behaviour is expected to be more important than on the atomic length scale. On the other hand, due to the de Gennes type narrowing effect [10] the α relaxation in this q range is much slower at the same temperature than at other q and therefore well separated in time from the β process over a larger temperature domain. This allows us to determine the amplitude of the α process, identified with the MCT non-ergodicity parameter $f_q(T)$, directly from the experimental data, without model fitting. Indeed, curve (a) in figure 7 shows the time relaxation behaviour at the pre-peak position at the highest temperature in our study. By identifying the amplitude of the α process with the inflection point around 50 ps, we might make a systematic error of about 0.01, corresponding to the extrapolation to $t = 0$ of the observed von Schweindler type relaxation between 50 and 1000 ps with an exponent of 0.6. At 385 K and below, $I(q, t)$ is constant over this time interval within the experimental precision of 0.005–0.01 at all q between 0.6 and 1 Å^{-1}. Note that due to the lack of multiple scattering corrections [10] underestimates the slowing down effect. Analysis of our present data suggest that the effective α relaxation time is about six times shorter at $q = 1.8$ Å^{-1} than at $q = 0.8$ Å^{-1}, in contrast to the factor of about three reported in [10]. The current NSE experiments were performed using the NSE spectrometer IN11C at ILL, and a detailed account will be published elsewhere [11].

The q range around 0.2–0.8 Å^{-1} has previously been also explored by NSE spectroscopy in a large number of glasses, including CKN [10]. Correction for multiple scattering has not been performed in any of the previous NSE experiments. As a matter of fact, MS contamination is indeed much less important in this kind of study than what we have seen above for inelastic work, since the relevant structure factor $S(q, 0)$ increases less rapidly with q than $S(q, \omega)$, cf figures 1, 3 and 5.

Nevertheless MS still leads to substantial distortions of the results. We have now determined, that in our 3 mm thick CKN sample at 6 Å incoming wavelength 31% of the measured quasielastic intensity at $q = 0.8$ Å^{-1} is double scattering with q around the main peak in $S(q)$. We have therefore, for the first time in NSE spectroscopy, implemented corrections for multiple scattering effects, using the above described method of combination of numerical simulation and taking data several wavelengths. Our analysis shows that multiple scattering substantially distorts the spectra, e.g. it leads to errors ranging from 0.06 to 0.13 in the 50 to 1000 ps time range for curve (a) in figure 7.

In our current search for a direct signature of a critical temperature we have studied the temperature and wave number of dependence of the amplitude of the α relaxation $f_q(T)$ at temperatures up to 400 K. Part of the results is shown in figure 8. As mentioned above, the as measured NSE spectra miss much of the vibrational contributions to $I(q, t)$, therefore we have chosen to determine the relative change of $f_q(T)$ only with respect to $f_q(T = 290$ K$)$. This ratio is much less influenced by the missing phonon-like scattering, actually only within
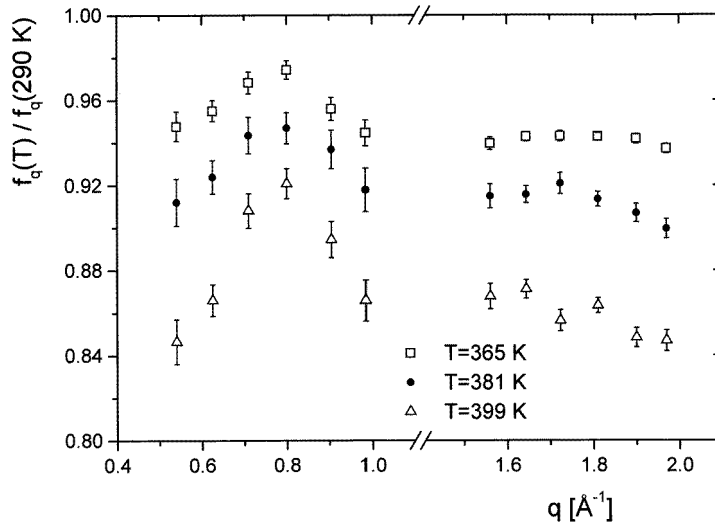
Figure 8. Amplitude of the α relaxation step (non-ergodicity parameter) normalized to its measured value at room temperature as a function of temperature T and wavenumber q. The maximum of the de Gennes type narrowing is accompanied by a maximum in the variation of this amplitude with q.

the error at $q < 1$ Å^{-1} and to about 6% at the highest temperature at higher q. The only role of these higher q data in our analysis is to allow us to perform the multiple scattering correction on the quasielastic signal, which in turn is measured without any systematic error by NSE. The results in figure 8 confirm earlier findings that $f_q(T)$ has a maximum at the pre-peak position, 0.8 Å^{-1}, which correlates with the maximum of the de Gennes type narrowing effect in the α relaxation. This also implies that the relative weight of the β process is minimal at this point. This is consistent with the conclusions from the direct observation of the β process, as discussed in the previous section in connection with figure 5.

The precise temperature dependence of $f_q(T)$ in the q range 0.54–0.98 Å^{-1} is shown in figure 9. In order to improve the statistical accuracy, we have taken the weighted average of all data within this q range. These data correspond to the directly measured NSE signal and the maximum possible systematic error at 400 K is still less than 1%, as discussed above in connection with figure 7. The arrow in figure 9 indicates the suspected position of T_c, as previously found [12] by examining potential compatibility between experiment and MCT. We observe no sign of the predicted crossover to a temperature independent $f_q(T)$ above this or any other critical temperature below 395 K. This actually rules out the existence of T_c in CKN, since the consistency with other MCT predictions sets an upper limit close to the value shown in figure 9 [12]. On the basis of this result we believe that previously reported evidence for the existence of a MCT type critical temperature in various fragile glasses might have been contingent on details of fitting to models and there is an urgent need for performing further model independent studies.

6. Conclusions

Inelastic neutron scattering has been extensively used in the past decade in the study of the physics of liquids and glasses, in order to explore dynamical processes in space and time on the
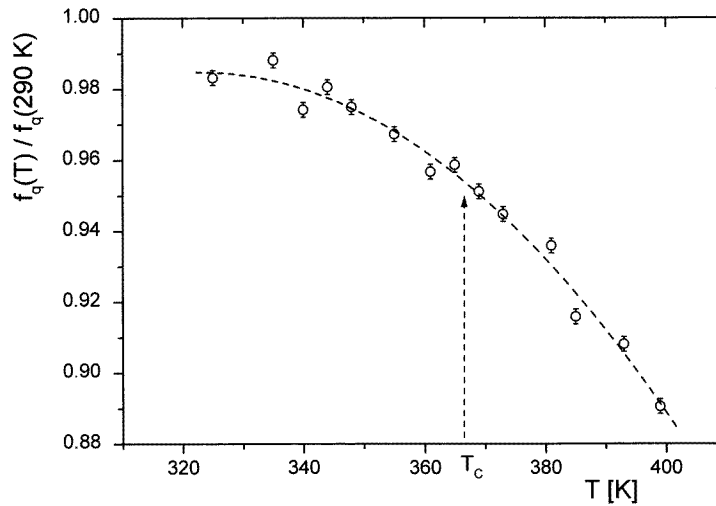
Figure 9. Temperature dependence of the non-ergodicity parameter averaged for better statistical accuracy over the q range 0.54–0.98 Å^{-1}. The arrow indicates the temperature previously inferred from less direct data (see text) as a candidate for T_c. In contrast, no sign of a singularity is apparent in the present, more accurate data.

microscopic scale. These kinds of study, while very successful in many respects, have been handicapped by being limited in the range of accessible wave numbers to q values close to the main peak of the structure factor and above. (In real space this corresponds to the exploration of nearest neighbour and shorter distances.) At smaller q the inelastic scattering intensities are small and overwhelming multiple scattering effects made meaningful analysis of experimental data impossible. We have developed a numerical simulation aided experimental strategy which allows us to obtain reliable inelastic scattering information for wave numbers several times smaller than previously accessible. In real space the new range corresponds to that of the intermediate range order in many glasses, i.e. several times the atomic spacing. On this length scale collective aspects of the dynamics are expected to be more apparent, as illustrated by the discovery many years ago that structural correlations in a supercooled liquid are dramatically longer lived in this range than on any other length scale. Our detailed study of the intermediate length scale dynamics in the archetypal fragile glass former CKN lead us to two fundamental conclusions: (a) the structural relaxation process in the supercooled liquid takes place in two stages in time and (b) there is no signature of a critical temperature above the glass temperature T_g.

Observation (a) is the first direct experimental evidence for a most central prediction of mode coupling theories, namely the existence of a fast structural relaxation step, also referred to as the MCT β process, in addition to the well understood 'slow' (α) process governed by the viscosity. Our finding thus contradicts conventional wisdom, which has assigned the experimental feature identified with the β process to the emergence of additional vibrational modes in the meV energy range or to atoms 'rattling in the cage'. It rather appears that the real nature of the 'cage effect' is the survival of the vibrational modes of the solid glass phase without essential modification in the supercooled liquid phase as long as the slowness of atomic diffusion makes the local instantaneous structure (very similar in the two phases) survive for times long compared to the frequency of the vibrations.

Our conclusion (b) is based on a direct, model independent, observation of the temperature dependence of the amplitude of the α structural relaxation process, defined as the non-ergodicity

parameter in MCT. This can only be accomplished in the q range of the intermediate range order, where the α relaxation is much slower and therefore better separated from the fast (β) stage. Evidence previously reported by several groups for the existence of a singularity in the temperature dependence of the non-ergodicity parameter, indicative of a critical temperature theoretically predicted by MCT, involved model dependent data analysis. Our model independent results contradict these claims, suggesting that they were artificial consequences of the necessity to use model assumptions for interpreting previous experimental data. In view of the great similarity of behaviour generally found between more or less fragile glasses, one can ask the question whether the absence of a singular point T_c only applies to CKN or more generally. This deviation from MCT predictions is not necessarily incompatible with the basic mechanism proposed by these theories. The temperature dependence of the coupling parameters might follow a more complex scenario than the one phenomenologically assumed in the theory and actually there might be a fundamental physical reason for an evolution with decreasing temperatures that avoids singularities.

Acknowledgments

References

[1] Carpenter J M and Pelizzari C A 1975 *Phys. Rev.* B **12** 2391
[2] Mezei F 1991 *Liquids, Freezing and Glass Transition* ed J P Hansen, D Levesque and J Zinn-Justin (Amsterdam: North-Holland) p 629
[3] Kartini E, Collins M F, Collier B, Mezei F and Svensson E S 1996 *Phys. Rev.* B **54** 6292
[4] Wilson M and Madden P A 1999 *J. Phys.: Condens. Matter* **11** 237
[5] Russina M, Mezei F and Lechner R to be published
[6] Sokolov A P, Rössler E, Kisliuk A and Quittmann D 1993 *Phys. Rev. Lett.* **71** 2062
[7] Götze W 1985 *Z. Phys.* B **60** 195
     Götze W and Sjögren L 1992 *Rep. Prog. Phys.* **55** 242
[8] Ngai K L 1993 *J. Chem. Phys.* **98** 7588
[9] Buchenau U, Wischnewski A, Richter D and Frick B 1996 *Phys. Rev. Lett.* **77** 4035
[10] Mezei F, Knaak W and Farago B 1987 *Phys. Scr.* T **19** 363
[11] Mezei F, Russina M and Farago B to be published
[12] Mezei F 1989 *Dynamics of Disordered Materials* ed D Richter *et al* (Berlin: Springer) p 164